

REMARKS ON THE THERMAL INVESTIGATION OF SEDIMENTARY ROCKS CONTAINING ORGANIC MATERIAL

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INTRODUCTION

In the investigation of sedimentary rocks containing clay minerals and carbonates, the determination of the amount and character of organic material present cannot be neglected. It seems to be essential to identify the organic components soluble in organic solvents as well as the insoluble ones especially from the point of view of hydrocarbon researches. Here it is not aimed to deal with the possibilities of instrumental investigations of separation and qualitative or quantitative determinations of different organic components present in the sediments, merely the question will be dealt with what kind of conclusions may be drawn from the character and position of exothermic peaks originated from the organic material and the DTA curves of sedimentary rocks and to what extent may these exothermic effects be used to the (at least qualitative) characterization of organic material present.

It is well known that the thermal effects of clay minerals are interfered by thermal effects from the combustion processes of the organic material since — without applying an inert atmosphere — the strong exothermic effect due to the combustion of the organic material is in the same temperature interval as the strong endothermic effect of clay minerals, first of all that of kaolinites.

The investigations were carried out with a „Derivatograph” constructed by PAULIK, F., PAULIK, J. and ERDEY, L. which renders possible to trace and record simultaneously *T*, *TG*, *DTG* and *DTA* curves.

Forms of appearance of organic material in sediments

According to HUNT and JAMIESON [1956] as well as HUNT and FORSMAN [1958] and other authors in the non-reservoir rocks the organic material may be present mainly in two forms:

a) organic compounds soluble in organic solvents as the paraffines, naphtenes and other N-S-O-containing organic compounds similar in composition to the heavier fraction of oil to be found in the reservoir rocks as well as the soluble bituminous components similar to those of the oil;

b) an insoluble organic material, the kerogen.

Samples of Lower Pannonian sedimentary rocks investigated are derived from the Algyó oil-field (near Szeged) and most of them contain organic material in some form if in fairly varying and small amounts as shown by chemical and DTA investigations. The petrographical investigation of thin sections of these rocks also show-

ed the presence of coalified plant remnants, some lignite and of remains of oil dried in the pores. Therefore it seemed to be purposeful to study the effect of combustion processes of different kinds of organic material exerted on the DTA curves.

General features of thermal effects of organic materials

The exothermic effect due to the combustion of the organic matter appears as a rule between 300—600 °C with a maximum at about 400° C the temperature of which, however, may be changed depending on the character of the organic material. The temperature of exothermic peaks characteristic of different coaly material (if the rock contains the given material in 5 per cent) is given by GRIMSHAW and ROBERTS [1957]. Thus, the temperature of the exothermic peak is at 389° C in the case of lignite, the temperature of the 1. exothermic peak is at 387° C and 485° C for the 2. exothermic peak in the case of oil shale whereas the first exothermic peak appears at 390° C in the case of bituminous coals. The position of this peak is independent either a low or middle or high rank bituminous coal is in question. The temperature of the second exothermic peak, however, increases in this series from 515° C to 524° C though this change is not a significant one.

From the point of view of thermal investigations the ratio of volatile and non-volatile carbon proves to be interesting and essential. The ratio of non-volatile carbon to the total carbon in oil shales and lignite amounts to 35% and 54%, respectively, depending on whether they contain a significant amount of components richer in carboxyl- and hydroxyl-groups, while the amount of non-volatile carbon reaches 85 per cent and 96 per cent, respectively, in the bituminous coals and the anthracite.

The shift of ratio of volatile and non-volatile carbon exerts an essential influence on the temperature of the exothermic peak of the DTA curve, namely, the first peak appearing between 350—390° C may be taken as originated from organic compounds richer in hydroxyl- or other oxygen-containing groups whereas the second exothermic peak at higher temperatures represents the combustion of non-volatile carbon and at an even higher temperature occurs the combustion of elemental carbon. E. g. according to GRIMSHAW and ROBERTS [1957] the temperature of the exothermic peak is at 564° C in the case of anthracite and 613° C of graphite.

EXPERIMENTAL PART

Types of exothermic peaks in the DTA curves of samples investigated

While examining the character of exothermic peaks between 300—520° C on derivatograms of Lower-Pannonian sedimentary rock samples from Algyő some types of peaks may be distinguished emphasizing, however, that the single types don't mean a sharp separation, there exists a transition between the single types. The exothermic peak of *type 1* is characterized by the appearance at about 395—415° C of a well developed inflection instead of an expressed exothermic peak of lower temperature whereas the temperature of the 2nd well developed and dominant exothermic peak is at about 490—515° C.

The exothermic peak of *type 2* differs from the former essentially merely in the peak temperature and the 1 and 2 exothermic effects are more balanced. The first peak is at 350—375° C and the second — of similar intensity — at 470—475° C. The temperature of the peaks is in connection with the amount and the fineness of

distribution of organic material present. The lower is the concentration the lower will be the peak temperature.

The peak of *type 1* (Fig. 1) is registered on the DTA curve of a sample containing 3,15% organic material whereas that of the sample showing a peak of *type 2* only 0,75%.

In the case of peaks of *type 3* hardly any difference between the first and second exothermic effects can be stated. An exothermic effect reveals from 365° C to 475 °C.

The peak of *type 4* is essentially the contrary to type 2, namely, the first peak between 340—375° C is more expressed whereas the second one between 470—495° C is rather weak or sometimes hardly observable.

The organic matter content of a sample showing in its derivatogram a peak of type 3 was 0,92% and 0,87% of a sample showing on its DTA curve a peak of type 4.

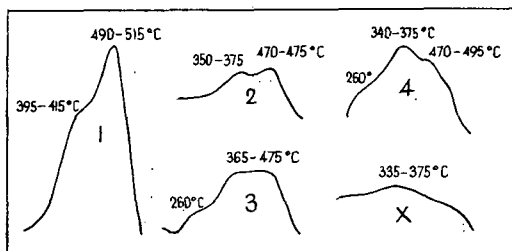


Fig. 1. Types of the exothermic DTA peaks originated by the organic material content of the samples.

Considering the frequency of exotherm peaks of various types peaks of type 3 and 4 proved to be the most frequent. Peaks of type 1 and 2 could be observed only on DTA curves of relatively few samples.

The question may arise whether or not is possible to draw some conclusions by model-experiments from the character of exothermic peaks on DTA curves of sediments containing organic material on the organic material present, taken as known the fact that the exothermic effect of lower temperature belongs to the combustion processes of organic components of higher volatility and the exothermic effect of higher temperature represents the combustion of components of lower volatility and the „fixed” carbon.

Thermal effects of organic materials extractable in organic solvents

Starting from the consideration that the samples investigated may contain soluble organic material similar to components of heavier fraction of oil — even more since the samples are derived from reservoir rocks — examinations were carried out concerning the effect of the oil and its single fraction, respectively, on the character of exothermic peaks observable on the DTA curves.

An oil sample from the Deszk-field was mixed in 5 per cent to Al_2O_3 and the derivatogram (T, TG, DTG, DTA) was taken, as shown in Fig. 2.

The very weak exothermic effect on the DTA curve at 150° C is probably in connection with components of higher volatility, followed by well developed exothermic peaks at 350 and 390° C, respectively and at last a well pronounced inflection may be registered at 500° C. The main maximum on the DTG curve is at 310° C (the first very weak maximum is at 70 °C) and the elongated very flat maximum on.

the DTG curve at about 500° C points to a process following the main reaction. The step on the TG curve, corresponding to the main reaction is between 150 and 420° C and the maximum of loss of weight is also in this temperature interval. The beginning and the end of the step on the TG curve is determined by the corresponding minima of the DTG curve.

In the described exothermic effect the complex effect of single fractions of oil is revealed, therefore, to study the single fractions on the DTA etc. curves, the oil sample was separated to six fractions by fractional distillation at atmospheric pressure.

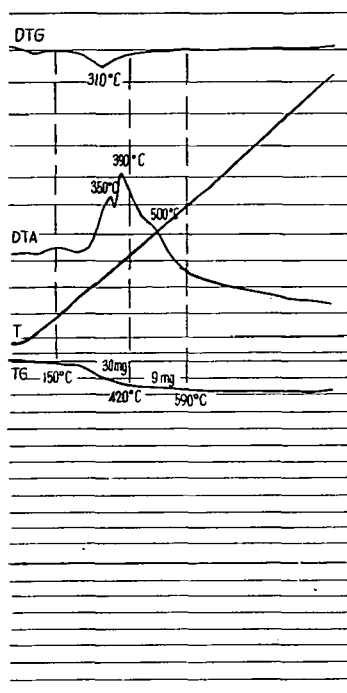


Fig. 2. Derivatogram of oil sample from Deszk (5 per cent oil soaked in Al_2O_3)

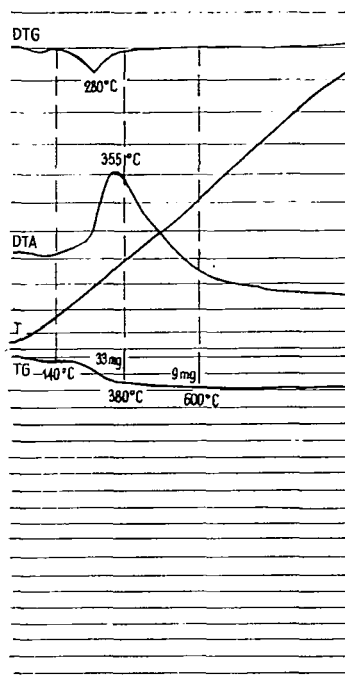


Fig. 3. Derivatogram of oil fraction distilled between 280–300° C (5 per cent in Al_2O_3)

TABLE I.

No. of fractions	Distillation temperature interval	Per cent	Remarks
1	—100	20,40	Dist. residue
2	100—200	8,65	
3	200—280	19,35	
4	280—300	21,75	
5	300—350	21,10	
6	350—	8,75	

To compare the effect of single fractions to that of the oil sample, 5—5 per cent from fractions 4 and 6 were mixed to Al_2O_3 . Their derivatogram is shown in Fig. 3 and 4.

Furthermore, a rock sample of relatively low (0,9 per cent) organic material content was chosen and of the oil fractions mentioned in Table I fractions No 3, 4, 5, and 6 were mixed to it in 0,5 and 3 per cent, respectively. In Figs. 5—8 are shown only mixtures containing 3 per cent of the fractions mentioned.

In general the following tendencies may be stated:

1. The maximum on the DTG curve preceded the temperature of the maximum (exothermic peak) on the DTA curve in the case of the different fractions and the most pronounced loss of weight on the TG curve belongs to this DTG maximum.

TABLE II

Beginning and end of TG steps belonging to the DTG maximum	Distillation temperature of the fractions
60—325° C	200—280° C
115—345° C	280—300
100—355° C	300—350
180—400° C	350° C

TABLE III

Distillation temperature °C	Amount of fraction in the rock sample per cent	Temperature of the DTG maximum °C
200—280	0,5	180
	1,0	
	3,0	200
280—300	0,5	230
	1,0	240
	3,0	260
300—350	0,5	240
	1,0	250
	3,0	290
350—	0,5	300
	1,0	310
	3,0	340

2. The temperature of the maximum on the DTG curve approaches more and more to the temperature of the exothermic effect on the DTA curve if fractions of higher boiling point and greater C-number are present. The higher is the distillation temperature of the fraction the higher is the temperature of the DTG maximum as shown in Fig. 9.

3. The temperature of the beginning and end of steps on the TG curve belonging to the loss of weight of the reaction indicated by the DTG maximum is also

influenced by the boiling point of the fraction. Higher boiling point, greater C number means the shift of this step to higher temperatures.

4. The temperature of the DTG maximum is influenced not only by the boiling point and composition of the fractions but also by the amount of the fractions.

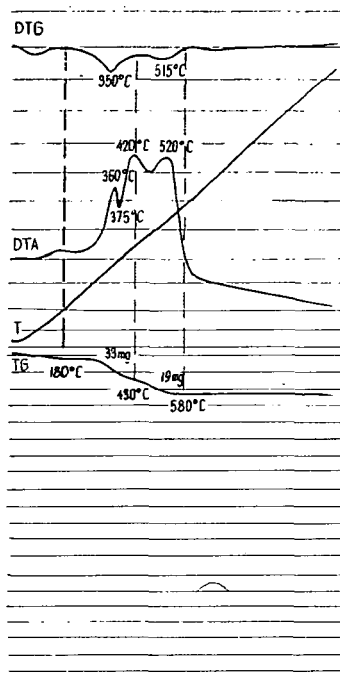


Fig. 4. Derivatogram of the oil distillation residue (after distillation at 350° C; 5 per cent in Al_2O_3)

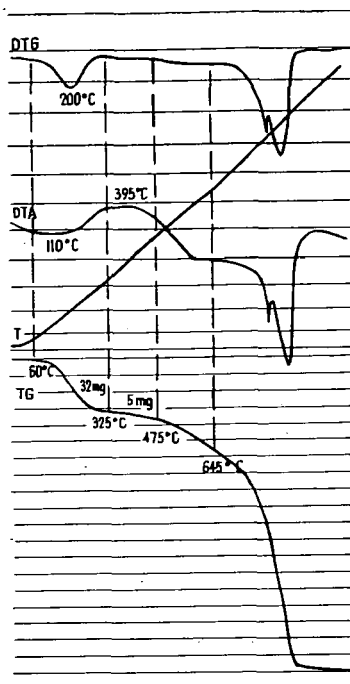


Fig. 5. Derivatogram of a sedimentary rock sample containing 3 per cent of oil fraction distilled between 200—280° C

weighed in. The lower is the temperature of the DTG maximum the smaller is within the same fraction the sample weighed in.

5. Similarly, the temperature of the main exothermic peak on the DTA curve rises by increasing the boiling point and the amount of fraction present as shown in Fig. 10 in the case of distillation residue, fraction 6.

The temperature of the DTA maximum in the case of fraction No 4 (distillation temperature interval 280—300° C) also increases corresponding to the increasing amount (0,5, 1,0 and 3,0 per cent) of the fraction present *i. e.* the peak temperature is 370—380—425° C.

6. Comparing the exothermic effects derived from the combustion at a higher temperature of components in derivatograms shown in Fig. 4 and 8 the mutual interference of the organic material and clay minerals is striking. Fig. 4 shows the derivatogram of Al_2O_3 with 5 per cent oil distillation residue (the residue after distillation at 350° C) and Fig. 8 the derivatogram of a rock sample containing some clay mineral and 3 per cent of the same oil fraction. On the derivatogram of the

rock sample the exothermic effect of higher temperature deriving from the distillation residue appears merely as a not well defined inflection at about 500° C.

Comparing derivatograms of Figs. 2, 3 and 4 the DTG maximum on the derivatogram of the original oil sample (Fig. 2) is at 310° C, in the case of distillation fraction No 4 at 280° C (Fig. 3) and at last at 350° C on the derivatogram of the distillation residue (Fig. 4). In the exothermic effect of the original oil sample the common effects of components of lower and higher boiling point appear. According to Table I, however, in the original oil sample fraction No 6 amounts to merely

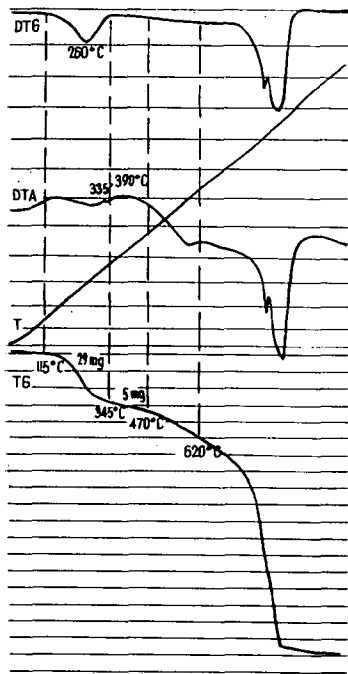


Fig. 6. Derivatogram of a sedimentary rock sample containing 3 per cent oil fraction distilled between 280—300° C

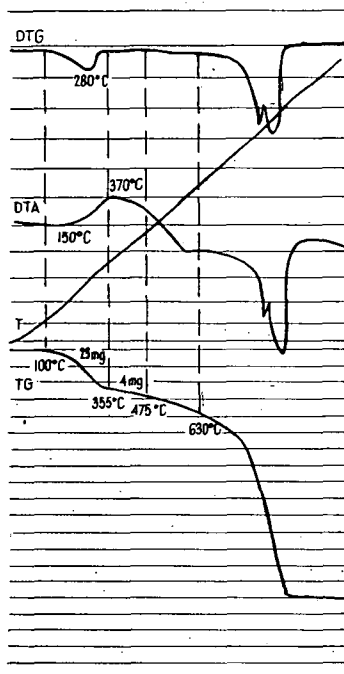


Fig. 7. Derivatogram of a sedimentary rock sample containing 3 per cent oil fraction distilled between 300—350° C

8,75 per cent, hence, the exothermic effect attributable to this fraction at 500° C appears only as a weak inflection. On the contrary, on the derivatogram of fraction No 6 a further well developed exothermic effect appears at 515° C which could hardly be observed on the derivatogram of the original oil sample at 500° C and did not appear on the derivatogram of the lower fractions. The increasing ratio of components of higher boiling point involves that the loss of weight measurable on the TG curve becomes more considerable also in a higher temperature interval (430—580° C) whereas in the case of fractions of lower boiling point the loss of weight is dominant in a lower temperature interval (60—400° C).

Remarks mentioned above may promote at least the qualitative interpretation of exothermic effects appearing on the derivatogram of sedimentary rocks containing soluble hydrocarbons, however, the thermal effect of the insoluble organic matter cannot either be neglected.

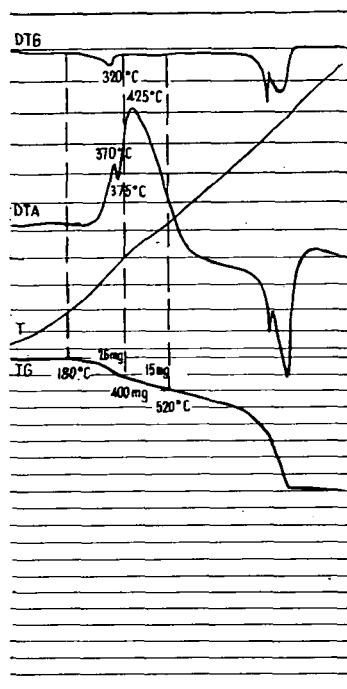


Fig. 8. Derivatogram of a sedimentary rock sample containing 3 per cent distillation residue

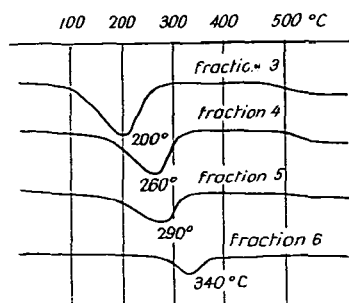


Fig. 9. Shift of the DTG maxima in the case of the successive distillation fractions

Thermal effects of insoluble organic materials (kerogen, lignite)

From one of our samples relatively rich in organic matter after extracting the soluble organic compounds, kerogen was isolated according to the method proposed by FORSMAN and HUNT [1958]. The organic carbon content of the sample amounted to 2,60 per cent corresponding to 3,15 per cent total organic material, after having been multiplied by 1,21, the organic factor calculated by the authors mentioned.

The C/H ratio of the kerogen isolated from the sample proved to be 14,3, very close to that of the fine kerogen fraction of the Wilcox-shale (14,7) as it is given the paper of FORSMAN and HUNT. For the sake of comparison, the C/H ratio in the oil fraction No 6, *i. e.* in the residue after distillation at 350° C, was 7,4.

The derivatogram of the kerogen isolated is shown in Fig. 11.

The similarity on the DTA curve between the character of the exothermic effect of the kerogen sample and the exothermic peak of type 1 observed on the derivatogram of the different original rock samples is striking. A very little difference

can, however, be stated, namely, on the DTA curve of the isolated kerogen a definite inflexion appears at about 360° C and the maximum of the peak is at 470° C whereas on the derivatogram of the original sample — from which the kerogen was isolated — the inflexion is at 395° C and the peak maximum at 510° C. In the case of the isolated kerogen the maximum on the DTG curve, attributable to the organic material, is at 445° C, and in the case of the original sample at 480° C. On the TG curve the main step corresponding to the loss of weight is between 280—525° C in the case of kerogen, and between 270—380° C in the case of the original rock sample.

If only 5 per cent kerogen was mixed to the rock sample, the inflexion on the DTA curve appears also at 360° C (as in the presence of 10 per cent kerogen) the peak maximum is somewhat lower: at 460° C, the DTG maximum at 440° C and the main loss of weight step in the TG curve is between 280—520° C i. e. a little lower than in the case of 10 per cent kerogen + 90 per cent Al_2O_3 mixture.

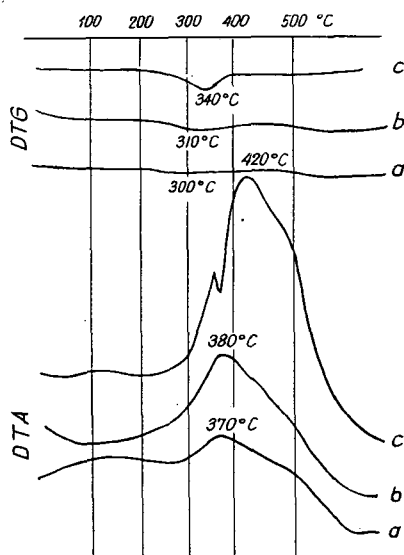


Fig. 10. DTA and DTG effects of the oil distillation residue mixed to rock sample if the residue amounts to a) 0,5 per cent; b) 1 per cent and c) 3 per cent

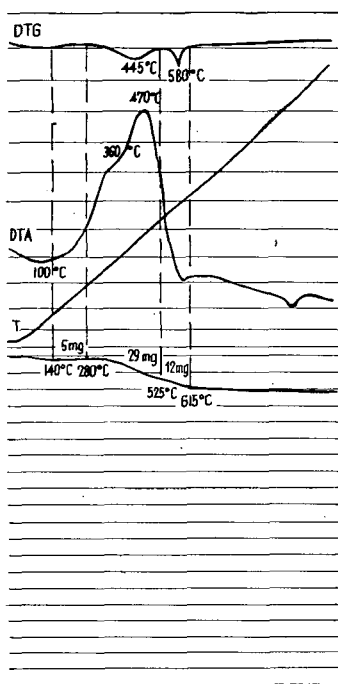


Fig. 11. Derivatogram of kerogen isolated from Lower Pannonian sandstone (10 per cent kerogen in Al_2O_3)

For information on the effect of coaly remnants on the derivatogram under the conditions of the investigations applied, 5 per cent lignit powder was mixed to Al_2O_3 and 10 per cent to a rock sample relatively poor in organic material. The derivatograms are shown in Figs. 12 and 13.

In the course of thermal investigations of coals, WELTNER [1965] as well as BÁTOR and WELTNER [1965] stated that on the DTG curve two maxima appear,

the lower temperature maximum above 200° C corresponds to the combustion processes of compounds of higher volatility and the higher maximum at about 350—400° C can be attributed to the combustion of the components of lower volatility + the „fixed” carbon. According to the authors mentioned, the greater the grade of coalification the lower the first effect and more expressed the second peak of higher tem-

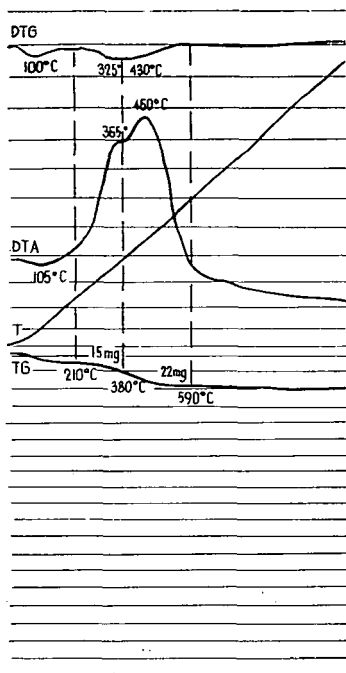


Fig. 12. Derivatogram of lignite (5 per cent in Al_2O_3)

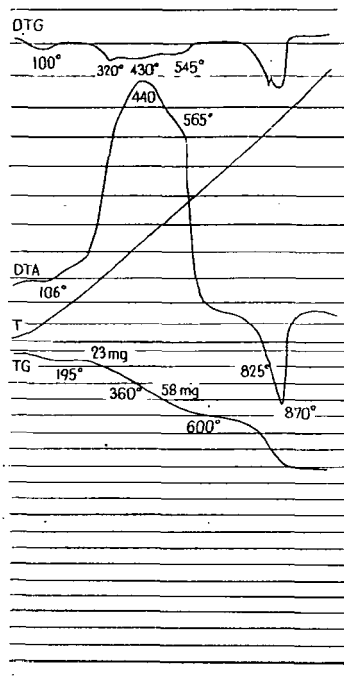


Fig. 13. Derivatogram of lignite (10 per cent in a rock sample)

perature whereas at a lower degree of coalification the first effect seems to be more intensive. This remark concerning the DTG maxima totally agrees with the statement of GRIMSHAW and ROBERTS referred previously. According to these authors the exothermic peak on the DTA curve appears at 390° C in the case of lignite whereas the DTA curve of bituminous coals shows two exothermic peaks; the first at 390° C and the second at 500° C. As the volatile content increases *i. e.* in the case of high rank coals towards the direction anthracite—graphite the first effect disappears and the intensity of the second peak of higher temperature will be dominating.

It is to be added that the peak-temperature is influenced not only by the ratio of components of higher or lower volatility but also by the amount of the components present as shown in Figs. 9 and 10.

Comparing the derivatograms of kerogen isolated and the lignite the following statement may be drawn:

1. The type of the DTA effect is the same and corresponds to the exothermic peak of type 1 (Fig. 1).

2. The DTG curve of the kerogen shows only one maximum at about 440—445° C whereas on the DTG curve of the lignite disregarding the maximum at 100° C two maxima appear at 320—325° C and 420—430° C originated by overlapping reactions.
3. Corresponding to the one DTG maximum, the main loss of weight step on the TG curve is between 280—525° C in the case of kerogen whereas in that of the lignite two steps may be distinguished on the TG curve corresponding to the double DTG maxima, the first between 210—380° C and the second between 380—590° C and the latter means the greater loss of

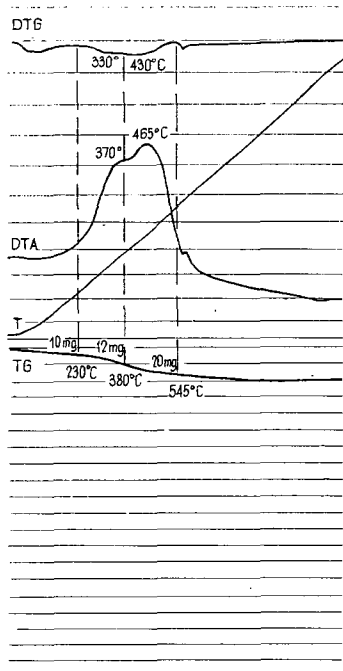


Fig. 14. Derivatogram of a mixture of 2,5 per cent kerogen — 2,5 per cent lignite — 95 per cent Al_2O_3

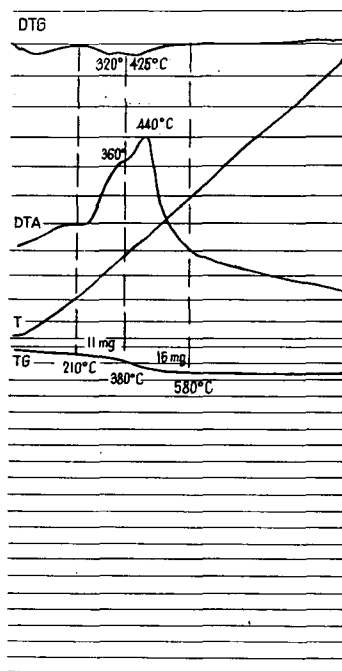


Fig. 15. Derivatogram of a mixture of 1 per cent kerogen — 3 per cent lignite — 96 per cent Al_2O_3

weight. In the presence of clay minerals, however, this second step originated by the combustion of organic material cannot agreeably be distinguished by the overlapping step originated by the decomposition of the clay minerals as in the presence of organic material and clay minerals both the exothermic effect of the organic material and the following endothermic effect of the clay minerals on the DTA curve will also be distorted (Fig. 13) and on the DTG curve after the maximum at 320° C and 420° C another maximum appears at 545° C attributable to the decomposition of the clay minerals and partly overlapping the second maximum.

Thermal effects in joint presence of different organic substances

Derivatograms of mixtures of kerogen — lignite and oil—lignite (all the components mixed to Al_2O_3 in various ratios) were also studied as shown in Figs. 14—17. Considering the derivatograms the following statements can be established.

1. On the DTG curve of different mixtures in the presence of lignite its characteristic two maxima appear at 300—330° C and at 420—440° C, respectively, disregarding whether oil or kerogen was the other component beside lignite.

2. The exothermic DTA effect on the derivatogram of the kerogen — lignite mixtures corresponds to the peak of type 1, and the temperature of the DTA and DTG maxima is influenced by the kerogen/lignite ratio, by decreasing the kerogen content the temperature of both maxima will somewhat be lowered.

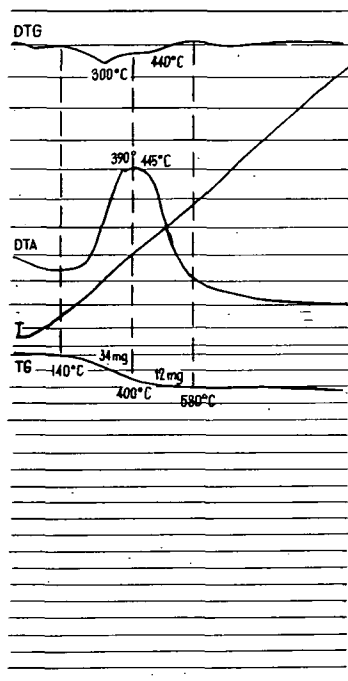


Fig. 16. Derivatogram of a mixture of 4 per cent oil — 1 per cent lignite — 95 per cent Al_2O_3

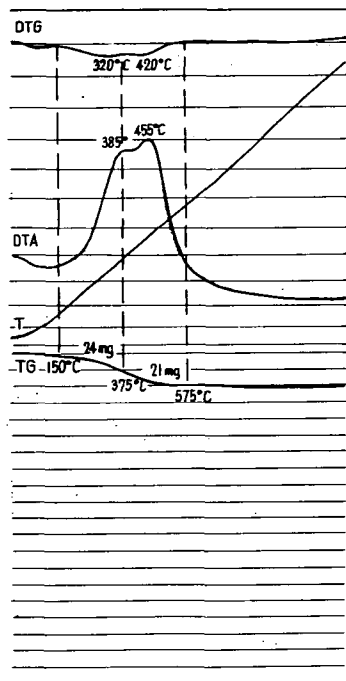


Fig. 17. Derivatogram of a mixture of 2,5 per cent oil — 2,5 per cent lignite — 95 per cent Al_2O_3

3. In connection with the two DTG maxima originated by overlapping reactions as mentioned in the case of pure lignite, the loss of weight represented by the TG curve can also be divided into two steps, the first starts at 210—230° C and the second from 380° C and ends at 545—580° C. The relatively greater loss of weight is represented by the second step at higher temperature pointing to that the components of lower volatility + the „fixed” carbon play a greater role than the highly volatile components.

While interpreting the exothermic effects of kerogen-lignite mixtures the following are to be taken into consideration:

It is mentioned by FORSMAN [1963] in his paper dealing with the geochemistry of kerogen that generally three types of kerogen can be distinguished on the basis of investigating its oxidation processes. The first type of kerogen resembles of humic material playing a role in lignites, peats, and coals, too, the second type may be taken of algal origin whereas the origin of the third type is questionable, however, in the course of pyrolysis this type also produces oil.

On the basis of the great similarity of the DTA effects of the lignite sample investigated and the kerogen isolated from the rock sample, disregarding the differences in peak temperatures, it may be supposed that the kerogen investigated may be considered as belonging to the first type according to FORSMAN's grouping.

According to BREGER and WHITEHEAD [1951] the degradation of the lignin is indicated by the intensive exothermic peak at 425° C. On examining the derivatograms of lignite or kerogen or mixtures of the two components it may be stated that the peak temperature is shifted towards higher temperatures in the presence of kerogen. This fact may presumably be interpreted that the devolatilization of the humic matter occurs and compounds of higher stability are formed by polymerisation or condensation or such are already present in the kerogen, the degradation of which occurs only at higher temperature.

4. In the case of oil and lignite mixtures by decreasing the oil ratio rather the exothermic peak of type 2 appears whereas by increasing the amount of oil relating at least to the amount of lignite, the difference between the two peaks in the exothermic DTA effect nearly totally disappears thus the effect will be very similar to the peak of type 3.

5. On the DTG curve of oil-lignite mixtures also two maxima appear at 300—320° C and 420—440° C, respectively, as a result of succeeding and partly overlapping reactions. By increasing the oil ratio the first reaction and the DTG maximum corresponding to it will be more expressed, consequently, the loss of weight recorded by the step on the TG curve between 140—400° C will be dominating. (The derivatogram of the oil used is shown in Fig. 2) The loss of weight in the temperature interval mentioned may be attributed to the components combustible at a lower temperature, introduced into the mixture in a greater amount by adding oil to it. By decreasing the oil ratio the two maxima on the DTG curve will be more balanced and the two steps on the TG curve at 150—375° C 375—575° C approach each other.

SUMMARY

a) On the derivatogram of the kerogen only one DTG maximum appears, on the other hand, on the DTA curve the main exothermic effect appears at 460—475° C after the inflection at 350° C. The main step on the TG curve, corresponding to the loss of weight, occupies the smallest temperature interval from 280° C till 500—525° C among all materials and mixtures investigated.

b) It is characteristic of lignite that two DTG maxima can be observed disregarding the maximum at about 100° C due to dehydration; the maximum of lower temperature is at 320—325° C, the other one of higher temperature at 420—430° C somewhat lower than the single maximum of kerogen. Corresponding to the double DTG maxima, on the TG curve two definite steps can be distinguished covering together a greater temperature interval than in the case of kerogen. The loss of weight starts already at about 195—210° C and the second step begins at 360—380° C and terminates at 590—605° C. The character of the exothermic effect on the DTA

curve is similar to that of the kerogen isolated by the authors at least in the case of the lignite sample used for comparison. The inflexion point is at 365—375° C as in the exothermic effect of the kerogen, the temperature of the main exothermic peak is somewhat lower, 440—450° C.

c) Considering the derivatogram of the oil sample a pronounced DTG maximum can be observed at an essentially lower temperature (310° C) than that of the kerogen, however, nearly equals with the temperature of the lower temperature DTG maximum of the lignite. The loss of weight step starts at an essentially lower temperature than with kerogen and lignite, at about 140—150° C pointing to the loss of lower boiling point components of the oil. Corresponding to the heavier, bituminous components of the oil, an observable second DTG maximum also appears and in connection with it a second step on the TG curve pointing to the very small loss of weight can also be observed. This second step on the TG curve and the DTG maximum, respectively, appear definitely merely on the derivatogram of the distillation residue of the oil (residue after distillation at 350° C). Its derivatogram shows already two pronounced DTG maxima at 350° C and 515° C.

d) Kerogen being present beside the lignite and oil beside lignite, respectively the main characteristics of these components as summarized above are reflected together on the derivatogram depending upon the quantitative relations. It is characteristic in the presence of oil that the step on the TG curve starts at a lower temperature than in the case of pure lignite or kerogen, hence, the first DTG maximum appears also at a lower temperature, thus, if a step of considerable loss of weight starts already at 200°C on the derivatogram of a sedimentary rock, the presence of oil traces may be supposed and if a second step can be observed on the TG curve and correspondingly two DTG maxima and the second TG step ends above 550—570°C, the presence of lignite can presumably be considered.

From the model-experiments outlined it may be concluded that by the differential thermal analysis of sedimentary rocks containing organic matter, the comparison of the character and temperature of effects appearing on the DTA and DTG curves as well the steps on the TG curves render possible to approach at least qualitatively the character of the organic material present.

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